Simulation of Carbon Nanotubes Growth by Laser Ablation

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Abstract: One of the synthesis methods of the single-walled carbon nanotubes (SWCNTs) is to use by laser ablation process. A simulation program was built to simulate the nucleation process of the carbon nanotubes. The simulation is based on the classical nucleation theory and the free energy of carbon nanotubes nucleus. In order to accurately simulate the growth of carbon nanotubes by laser ablation, the laser-material interaction in addition to the nucleation process must be considered. In this study the simulation is separated into two parts: laser ablation and Nucleation. The laser ablation process includes the heat transfer within the target leading to ablation. Then the nucleation process will be described using classical nucleation theory. The simulation results showed the diameters distributions of carbon nanotubes are around (1-1.7) nm over all temperatures. Comparison between the experimental and simulation results showed there is a good agreement in their behavior.

Keywords: Carbon nanotubes; Laser ablation; simulation.

1. Introduction

The first MWCNTs were discovered by Iijima in 1991 when he found layers of rolled graphene structure in the soot of electric arc discharge method. Carbon nanotubes are cylindrical structure formed by rolling single layer or multilayers of graphene sheets into cylinder [1]. In 1993, Bethune group at IBM [2] and Iijima group at NEC [3] reported the synthesis of Single-Walled Carbon Nanotubes (SWNTs). The pulsed laser-ablation process for the production of single-wall carbon nanotubes was developed by Guo et al. [4, 7] at Rice University. Other improvements were made by Thess et al., [5] and and Rao et al., [6]. Laser ablation method uses a high-power laser (YAG type) to vaporize pure graphite targets inside a furnace at 1200 ± 3°C under an Ar atmosphere to produce MWNTs [7]. SWCNTs with purity as high as 90% can be produced by laser ablation technique which are purer than CNTs produced by arc discharge [8]. In general, the most commonly used catalysts are Ni, Co, and Fe. These are used independently or mixed with another metal. [9]

M. H. Rummeli (2010). The properties of CNTs prepared by the pulsed laser deposition process are strongly dependent on many parameters such as: the laser properties (energy fluence, peak power, CW versus pulse, repetition rate and oscillation wavelength), the composition of the target material, the inert gas pressure, the substrate and ambient temperature and the distance between the target and the substrates [10]. In 1995 Guo et al., [4] were first to synthesis of SWCNTs by Laser ablation technique. Later on used two laser pulses 50ns to vaporize carbon target with a cobalt-nickel catalyst, and achieved 70-90% efficiency [11]. The atmospheric temperature controls the chemical reaction and the laser intensity affects the process by which the particles species ejected [12]. Laser ablation can be accomplished by Ablation of a graphite target using either a pulsed laser [4, 5] or a continuous laser [13].

In both cases, the nanotubes nucleate in the vapor phase, coalesce, get carried away by the flowing argon and condense downstream on the water-cooled copper collector. The soot contains amorphous carbon, metal particles, and CNTs [13]. In our previous work, CNTs were produced by laser ablation using two targets technique (graphite and Ni) instead of one target (Ni/graphite) to synthesis SWCNTs by laser ablation process [14]. The aim of this work is to simulate the growth of carbon nanotubes by laser ablation by considering laser-material interaction in addition to the nucleation process. The laser ablation process includes the heat transfer within the target leading to ablation. The nucleation process will be described using classical nucleation theory. This simulation was design to simulate the distribution of SWCNTs at different temperatures and then compare these results with the experimental result.

2. Laser Ablation with Nanosecond Laser

Laser ablation can be divided into three main process, bond breaking and plasma ignition, plasma expansion and cooling, and particle ejection and condensation [15]. During the plasma ignition process, the dominant mechanism is thermal vaporization: the temperature of the solid surface increases, and a well-defined phase transition occurs, from solid to liquid, liquid to vapor, and vapor to plasma [16]. Nano-sized particles will be formed from condensation of the vapor. Condensation starts when the vapor plumes temperature reaches the boiling temperature and stops at the condensation temperature of the material. Liquid ejection of particles can occur by high pressure gradient forces within the highly expanding vapor plume acting as the molten surface. Solid sample exfoliation can occur from the large thermal stress gradients of the fast heating
process; thermal stresses can break the sample into irregular shaped particles, ejecting them from the surface.

3. Nucleation and Growth of Carbon Nano-tubes

Carbon nanotubes formation and growth mechanism during the laser ablation process started by the formation of liquid nanoparticles of metal supersaturated with carbon. These nanoparticles originate from condensation of the metal plasma/vapor in the moderate temperature zone of the laser ablation chamber. During the nucleation the metal nanoparticles can incorporate large amount of carbon depending on the temperature and its size [17]. Through cooling the solubility limit of carbon in liquid nanoparticles is decreased and the carbon begin to segregate[18]. The segregation of carbon occurs via diffusion towards the particles surface. The occurrence of such segregation is supported by the absence of carbon inside nanoparticles after solidification. Then the carbon crystalize at the surface of nanoparticle according to the two competing transformation which lead to the formation of graphite sheet and to nucleation of single walled carbon nanotubes [19].

4. Computational Method

In order to accurately simulate the growth of carbon nanotubes by laser ablation, the laser-material interaction in addition to the nucleation process must be considered. In this study the simulation is separated into two parts: laser ablation and Nucleation. The laser ablation process includes the heat transfer within the target leading to ablation. The nucleation process will be described using classical nucleation theory.

4.1 Interaction of laser light with target surface

Interaction of laser light with target surface will increase the internal energy of the target. The mode of interaction is considered to be thermal i.e. the time scale of the process is much longer than the relaxing time of the excited electron (10^{-15}s). The heat transfer is modeled as having a local thermodynamic interaction and neglecting heat transfer by convection because the interaction related to the target [19].

\[ E_{\text{stored}} = (E_{\text{in}} - E_{\text{out}})_{\text{cond}} + (E_{\text{in}} - E_{\text{out}})_{\text{rad}} \]  

(1)

The radiation term in equation (1) can be separated into two parts, the surface radiation term as a boundary condition and the laser energy as a heat source. Re-writing the heat transfer by conduction into 1-D heat transfer by conduction as:

\[ \rho \frac{\partial (C_p T)}{\partial t} = \nabla (KT) + q + S \]  

(2)

where \( q \) = energy generation per unit volume, \( S \) = source term for energy required for phase change. For laser at 1064 nm, the absorption coefficient is \(<10^5 \text{cm}^{-1}\) so \( q \) is neglected [20]. Within the target there is no phase change and \( S \) is considered to be zero. The heat transfer within the target is given by

\[ \rho \frac{\partial (C_p T)}{\partial t} = \nabla (KT) \]  

(3)

The internal boundaries are kept at the initial temperature \( T(t) = T_{\text{initial}} \) at \( t = 0 \). The radiation boundary condition is given by:

\[ - \frac{\partial (KT)}{\partial n} = \varepsilon \sigma (T_{\text{surf}} - T^4) + q_{\text{laser}} \]  

(4)

The algorithm of the COMSOL Program is shown in Fig. 1

4.2 Nucleation and Growth of Carbon nano-tubes

To describe the nucleation of carbon nano-tubes mathematically various mechanisms for the formation of carbon filamentous deposit have been introduced. In the first group Baker et al [21] showed a mechanism include a stage of carbon dissolution that is independent of carbon source. The second mechanism is based on the diffusion of carbon at the surface of the metal particle rather than on the bulk diffusion of carbon through the catalyst particle [22-23]. The third mechanism is based on the catalyst particles take part only in the tube initiation process such that the increase in the thickness in the primary tube occurs without the further participation of the metal particle [24]. The fourth group based on small metal clusters activates SWCNTs by moving around the open tube tip and bonding carbon atoms from the gas phase. [25]. The fifth group proposed a model for the formation of cylindrical layers around a hollow core using a thermo dynamic approach [26]. For the purpose of this study the model proposed by Tibbets and modified by Vladimir et al [27] will be used on the nucleation of the carbon nano-tubes on a nickel nano-particle.

4.3 Thermodynamic Treatment

The nucleation of carbon is a core step for the formation of all types of carbon filament deposit. The critical size of carbon nucleus determines the type of carbon deposit because the size of the tube cannot be smaller than the critical size. When the critical size of the carbon is sufficiently small compared to the size of the metal particle this allow the formation of on nucleus several nuclei. These nuclei combines into small structure with the carbon atoms arranged in hexagons which transform into graphite sheet bonded with its edges to the metal surfaces [28-29]. The change in the free energy for the formation of two dimensions nucleus can be written using Gibbs free energy [30] as:

\[ \Delta G = \frac{\mu}{m} \Delta G_{\text{nucleus}} + \gamma l^2 (\sigma_{\text{nucleus - gas}} + \sigma_{\text{nucleus - surface}} - \sigma_{\text{surface - gas}}) + 10E_{\text{strain}} \]  

(5)
C N t C E N t
q h
\(-\) is a specific edge
m 4.5 h s has circular shape with
vi
ax
m h s\() \Delta \gamma \sigma \sigma \sigma \) \(- \Delta \gamma \sigma \sigma \sigma \) \(- \Delta \gamma \sigma \sigma \sigma \) 
9 s has circular shape with
after differentiation
\(- \) concentration of clusters
G k T k T
\(- \) strain at a given temperature equals
G k T k T
\(- \) strain arising from the bending of the
\(- \) graphene layer on the metal is given by \[32\]. Substitute in
\(- \) Eq. (5) to get the Gibbs free energy for the formation of
\(- \) nucleus with perimeter I and height h. After differentiation
\(- \) with respect to I , and rearrange to get I critical :
4.5 \(QIcEstrain h\) \(- \) free energy and E strain is a strain energy arising during the
bending of graphene layer on a metal. The change in
the free energy of nucleus \(\Delta G_{\text{nucleus}}\) is given by \[31\]:
\[\Delta G_{\text{nucleus}} = -k_b T \ln \left( \frac{a}{a_o} \right) = -k_b T \ln \left( \frac{x}{x_o} \right) \] (6)
where \(k_b\) is a Boltzmann constant, \(T\) is Temperature, \(a\) and
\(a_o\) are the carbon activities of the saturated and actual
solution respectively, \(x\) and \(x_o\) are the saturated and the
actual molar content of the dissolved carbon respectively
and \(Q_c\) is a constant ( for CNT it is equal to \(4.4\) ev). Use the
continuum formalism of elasticity, the strain energy
\((E_{\text{strain}} = \frac{Q_c I}{4.5h})\) arising from the bending of the
graphene layer on the metal is given by \[32\]. Substitute in
Eq. (5) to get the Gibbs free energy for the formation of
nucleus with perimeter I and height h. After differentiation
with respect to I , and rearrange to get I critical :
\(I_{\text{critical}} = \left[ \frac{\gamma h}{v m} \Delta G_{\text{nucleus}} + \gamma (\sigma_{\text{nucleus}} - \text{gas} + \sigma_{\text{nucleus}} - \text{surface} - \sigma_{\text{surface}} - \text{gas}) \right]^{1/2} \] (7)

The critical number of carbon atoms which can form a stable
nucleus can be calculated by substituting the total number of
carbon atom in nucleus \((n = \frac{\gamma I^2 h}{v m})\) in Eq. (7). If we
consider the nucleus has circular shape with \((I=2\pi r\) and
\(\gamma=1/4\pi) \[33\] then the critical size of the nucleus is given by
Eqs (8) and (9) :
\[n_{\text{critical}} = \left[ \frac{\gamma h}{v m} \Delta G_{\text{nucleus}} + \gamma (\sigma_{\text{nucleus}} - \text{gas} + \sigma_{\text{nucleus}} - \text{surface} - \sigma_{\text{surface}} - \text{gas}) \right]^{1/2} \] (8)
\[r_{\text{critical}} = -(\dot{\omega} + \frac{Q_c}{4.5h}) \left[ \frac{h}{v m} \Delta G_{\text{nucleus}} + (\sigma_{\text{nucleus}} - \text{gas} + \sigma_{\text{nucleus}} - \text{surface} - \sigma_{\text{surface}} - \text{gas})^{-1} \right] \] (9)
The critical radius in equation (9) means that the cluster that
has this critical size is energetically favorable to grow while
the smaller clusters will preferentially decay. For clusters
smaller than the critical cluster, the evaporation rate exceeds
the condensation rate and vice versa. An important
conclusion from the energy consideration is that the
evaporation rate of a cluster at a given temperature equals
the condensation rate of this cluster at the same temperature
and such a vapor pressure that the cluster is critical at it. The
condensation rate can be expressed by evaluating the
sticking cross-section. If \(N_i\) is the concentration of clusters
containing \(i\) monomers \((i\)-clusters\) the rate equation as
function of time can be written as follows:
\[\frac{dN_i}{dt} = C_i \cdot n_i \cdot (t) - (C_i + E_i) N_i \cdot (t) + \] (10)
\[E_i \cdot n_i \cdot (t); i = 2, 3, \ldots \]
Where \(C_i\) is the rate of monomer sticking with an \(i\)-cluster
or condensation rate, and \(E_i\) is the rate of monomer
evaporation from an \(i\)-cluster. Since the classical nucleation
theory considers only the initial stage of cluster
condensation, where the total cluster mass is small as
compared to the vapor mass, it is assumed that the monomer
concentration is constant \[34\], then \(\frac{dN_i}{dt} = 0\). To solve

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Eq. (10), it is assumed that clusters larger than J-cluster are instantly decomposed into monomers, so that
\[
\frac{dN_i(t)}{dt} = C_{i-1}N_{i-1}(t) - (C_i + E_i)N_i(t)
\]
(11)

To get an approximate analytical solution for steady state case using classical nucleation theory, rewrite equation (11) as [35]:
\[
\frac{dN_i(t)}{dt} = A_i(t) - A_i(t)
\]
(12)

Where \(A_i\) is the number of freshly formed i-cluster per unit volume and time and is given by
\[
A_i(t) = C_iN_i(t) - E_{i+1}N_{i+1}(t); i = 2,3,\ldots,J
\]
(13)

The number density of i-cluster at total equilibrium is
\[
(D_i) = N_i \exp(\frac{-\Delta G_i}{K T})
\]
The important feature of \(D_i\) is that for \(i > 1\)
\[
\frac{D_i}{D_{i+1}} \approx \frac{E_{i+1}}{C_i}
\]
(14)

Rewrite equation (13) using equation (12) as follows:
\[
A_{ss} \sum \frac{1}{C_iD_i} = \frac{N_i}{D_i}
\]
(15)

Where \(A_{ss}\) is steady state of i-cluster. For over all \(I\) Getting
\[
A_{ss} = \sum \frac{1}{C_iD_i} \approx \frac{1}{C_{ss}} \sum K_i \exp(\frac{-\Delta G_i}{K T})
\]
(17)

Where \(K_i = 4\pi R_i D_i\) is the attachment rate constant approximated by Park-Privman [36]. Where \(R_i\) is the radius of the single CNT \(R_i = R_i = 1.2 h_i^{1/3}\). The solute diffusion coefficient can be estimated by using Einstein formula for diffusion of cluster in the Argon gas [37] is
\[
D = \frac{k_B T}{6\pi \eta h}
\]
where \(\eta\) is the viscosity of Argon and it can be neglected [38]. For singlet carbon particle aggregates according to the difference between density of the primary nucleus formed and the rate of its transformation.
\[
\frac{dN_i}{dt} = \rho(t) - \sum_{j=2}^{\infty} \frac{dN_j}{dt}
\]
(18)

Where is the formation of critical nuclei in \(m^3/s\)
\[
\rho(t) = 4\pi h n_{critical} D^2 \exp\left( \frac{-\Delta G_{critical}}{K BT} \right)
\]
(19)

The concentration of carbon particle \((C(t))\) is a function of time and it decrease with formation and the growth of critical nuclei. Assuming the process of formation is irreversible the concentration as a function of time can then be written as [6]:
\[
\frac{dc}{dt} = -n_{critical} \rho(t)
\]
(20)

The master equation for population of large cluster \(i>3\) can be written as follows [39]:
\[
\frac{dN_i}{dt} = K_{i-1}N_{i-1} - k_i N_i^2
\]
(21)

To apply nucleation theory method numerically we used the following algorithm as shown in Fig.2.

5. Heat Transfer within Target

In the present work the heat transfer within target (graphite) due to the interaction of the laser beam with graphite under flowing of Argon gas and furnace temperature of 1000°C was introduced upon heat transfer within target Eq. (3). The laser source to perform laser ablation simulation was Nd:YAG with fluence of 1.5 J/cm², pulse duration = 10ns and wavelength = 1064 nm. The laser target has a dimension of \((10*10*0.3) \text{mm}^3\) with effective area \((2*2) \text{mm}^2\). The numerical procedure was developed under COMSOL MULTIPHYSICS Project ver (3.5).

The target was simplified to 2-D rectangle as shown as shown in Fig.3. The target was treated with mesh size (1nm) (boundary 3). Only the interface between heated and unheated target was solved i.e. a half of the target is irradiated by laser and the other half was not. Surface boundary condition for irradiated area (boundary 3 in Fig.3 is described by Eq.(4). The heated area (boundary 4) had the same equation as boundary 3 but without heat source distribution. Left bottom and right side (boundary 1, 2 and 5) are thermally insulated, adiabatic condition (\(n.K.N.T = 0\)). The computer program was run for physical time (10ns) pulse duration. The maximum time step was limited after several trial and errors to 2.5s*10^-13/s. The computational domain was taken as having area of 4mm² and depth of 3μm. The space step was taken to 10nm. As a result Fig. 4shows temperature field evolution of the target for time 10ns during laser action. Table 1 shows some global expressions and constants used in the simulation of the laser ablation.

![Fig. 3: Sketch of selected part of bulk sample for modeling in COMSOL with numbers of boundary conditions with material surface (dimensions in mm).](image-url)
Time step (dt) to calculate the population of clusters

Calculation of first concentration of C₃ cluster

Calculation of concentration of C₃ at dt

Calculation of production rate of critical particle at dt

Update of time step dt

Calculation of critical particle size

Calculation of production rate of critical particle

Update of time step dt

Open loop for number of nuclei n from 1-1000

Time step (dt) to calculate the population of clusters

Calculation of the population of clusters of n=1,2,3.. nuclei

Update of time step dt

Update of time step dt

Open loop to Calculate CNTs size distribution

Calculation of CNTs size distribution

Update

End
6. Carbon Nanotubes Formation

In the first step of nucleation process several carbon nuclei precipitate on the surface of the same metal surface (catalyst) and increase in diameter to form highly packed mosaic structure. If the nucleation rate is highly enough, the size of single wall nano-tubes tends toward minimal value that corresponds to critical nucleus. So that the first step in nucleation of carbon nano-tubes is estimation of critical nuclei ($n_c$). By using Eq. (8) the estimation of the critical nucleus in the range of (500-1400)$^\circ$K could be established which is typical for the formation of different catalytic carbon deposit. The numerical result for estimation of critical nucleus of carbon nano-tubes as a function of reaction temperature for Ni Catalyst is presented in Fig. 7. With increasing the temperature, the number of nuclei inside a critical cluster is decreased. Thus, with increasing the temperature the cluster size and also the diameter of the produced carbon nano-tubes are decreased. The probability of formation of SWCNTs is high at high temperature. The relation between the critical nuclei and critical radius for formation carbon nano-tube can be estimated using Eq. 9. The critical nucleus as a function of critical radius is shown in Fig. 8. It is clear from this figure the decrease of critical nuclei will decrease the critical cluster radius with increasing temperature.
Fig. 8: Critical nucleus of CNTs versus Critical radius (nm).

Fig. 9: Critical nucleus of CNTs versus Critical radius (nm).

Fig. 9: Critical nucleus of CNTs versus Critical radius (nm).

**Fig. 9:** Simulation results for carbon nanotubes distribution at different temperature (850-1000)°C. This simulation was designed to simulate the distribution of SWCNTs at different temperatures and then compare these results with the experimental results. The concentration of the solution is related to the C3 cluster which is (10^24)nm^-3.

Fig. 9: Simulation results for carbon nanotubes distribution at (a) 850, (b) 900 and (c) 1000°C.

From Fig 9 the diameters distributions of carbon nanotubes are around (1-1.7) nm over all temperatures. The yield of the nanotubes increased with increasing temperature. Finally the yield of the larger diameter increased as temperature increased. These results are reasonable if we consider that each temperature has its intrinsic n_c. Fig. 9 was then compared with the experimental distribution of SWCNTs at different temperatures Fig. 10 from our previous work [14] which gives the same behavior but with different yield value and the diameters of the nanotubes were around ~1(1-2)nm. This difference in the results between the simulation and the experimental work is resulted from the cluster formed after laser ablation is only C3 it contains C2, C and metal particle. In our previous work [14] it was found that at temperature between 750-800 °C the structure of the deposit carbon nanotubes has a web-like structure. At temperature 850°C - 1000°C there is a transformation of the deposit carbon nanotubes structure from web-like structure to spaghetti-like structure [14]. The temperature dependence of the carbon nanotubes diameter (nm) can be explained by changes in the cooling rate of the ablated carbon species. As the carbon vapor plume expands and cools down, the nanotubes structure become kinetically fixed [21]. As the nuclei size changes there is balance between the strain energy of the curved graphene sheet is and strain energy of an open graphene edge. A decrease in the nucleus diameter for fixed number of carbon atoms. Probably the nanotubes do not reach thermal equilibrium in rapidly expanding and cooling plume of carbon cluster [27].

Fig. 10: Experimental SEM image Histogram of carbon nanotubes distribution at 850°C ; 900°C and 1000 °C [14]

7. Conclusions

The production of the carbon nanotubes by using laser ablation is considered as an effective method for production of SWCNTs. In order to get best results in the simulation of carbon nanotube distribution is to take into account all types of clusters formed and the growth time of the nanotubes within these clusters.
References


